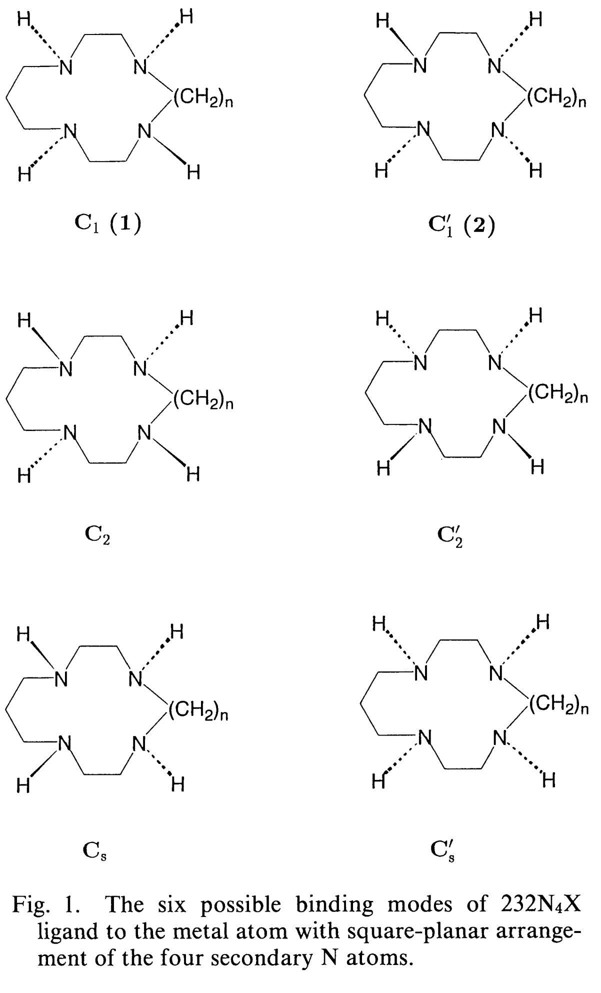
Bull. Chem. Soc. Jpn., **65**, 2114—2117 (1992) [Vol. 65, No. 8

X-Ray Structural Study of *trans*-$[CoCl_2(232N_415)]ClO_4$ ($232N_415$=1,4,8,11-Tetraazacyclotricosane)

Shigeki Kawano, Shigeru Ohba,* Masanobu Tsuchimoto,† and Junnosuke Fujita†
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223
†Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01
(Received March 12, 1992)

The structures of two isomers of *trans*-$[CoCl_2(232N_415)]^+$ in the perchlorate salt have been determined by single-crystal X-ray diffraction. Symmetry in the coordination of the macrocyclic ligand, $232N_415$, around the cobalt atom is absent for both isomers, and they are called C_1 and C_1' isomers. C_1 isomer, (**1**): monoclinic, space group $P2_1/n$, a=14.600(2), b=21.643(3), c=8.298(1) Å, β=100.78(1)°, V=2575.8(6) Å^3, Z=4, R=0.063 for 2446 observed unique reflections. C_1' isomer, (**2**): monoclinic, space group $P2_1/n$, a=19.579(2) b=7.423(1), c=19.636(2) Å, β=115.68(1)°, V=2571.9(4) Å^3, Z=4, R=0.068 for 2416 reflections. The fifteen-membered chelate ring takes a pseudo-skew form in **1** and a pseudo-envelope form in **2**, as the result of the different disposition of the C atoms bonded to two N atoms of the ring, **1** *trans* and **2** *cis*. The Co–N bond lengths in the fifteen-membered ring are from 2.011(6) to 2.026(9) Å, which are longer by ca. 0.05 Å than the other Co–N distances in the complex cations.

The macrocyclic tetradentate ligand, $232N_415$ forms 5,6,5, and 15-membered chelate rings with a metal atom. Six binding modes are possible for the macrocyclic ligand in square-planar arrangement of the four secondary N atoms as illustrated in Fig. 1. In preparation of the title *trans*-dichlorocobalt(III) complex, two isomers were obtained depending on the method of the synthesis.[1] The C_1 isomer was obtained by oxidizing a methanol solution containing $CoCl_2 \cdot 6H_2O$ and $232N_415$ with air, and the C_1' isomer was yielded by reaction of $[Co(CO_3)(232N_415)]^+$ with hydrochloric acid. Other isomers were not yielded. The crystal structures of the two isomers were determined to investigate the relationship between the molecular configurations and their relative stabilities.



C_1 (1) C_1' (2)
C_2 C_2'
C_s C_s'

Fig. 1. The six possible binding modes of $232N_4X$ ligand to the metal atom with square-planar arrangement of the four secondary N atoms.

Experimental

Green prismatic crystals were grown from methanol solutions. The densities were measured by flotation in a benzene–chloroform mixture. The X-ray intensities were measured up to $2\theta_{max}$=50° with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) on an automated Rigaku four-circle diffractometer AFC-5. The θ-2θ scan technique was employed at a scan rate of 6° min^{-1} in θ. The lattice constants were determined from 24 2θ values ($20<2\theta<28°$). Absorption correction was made by Gauss numerical integration method.[2] Systematic absences $h0l$, $h+l\neq 2n$; $0k0$, $k\neq 2n$ were observed for both **1** and **2**. The space group was uniquely determined to $P2_1/n$. The structures were solved by the heavy atom method. Non-hydrogen atoms were located in Fourier syntheses and were refined anisotropically. All the H atoms of **1** were included in the refinement. For **2**, only the H atoms bonded to N were introduced, because there exists positional disorder of the carbon atoms in fifteen-membered chelate ring. The function, $\sum w(|F_o|-|F_c|)^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least squares. Complex neutral-atom scattering factors were used.[3] The calculations were carried out on a FACOM M780/10 computer at Keio University using the computation program system UNICS-III.[4] The atomic parameters are listed in Table 2, the selected bond lengths and bond angles in Table 3, and hydrogen bonds in Table 4.[5]

Table 1. Crystal Data, Experimental Conditions, and Refinement Details for *trans*-[$CoCl_2(C_{19}H_{42}N_4)$]ClO_4 (F.W.=555.9)

	1	**2**
Isomer	C_1	C_1'
Space group and Z	$P2_1/n$, 4	$P2_1/n$, 4
D_m and D_x/Mg m^{-3}	1.44(2), 1.43	1.44(2), 1.44
μ(Mo $K\alpha$)/mm^{-1}	1.01	1.01
Color of crystals	Green	Green
Size of specimen/mm^3	0.20×0.20×0.50	0.18×0.32×0.45
Laue group	$2/m$	$2/m$
Range of h, k, and l	$-17 \leqq h \leqq 17$	$0 \leqq h \leqq 23$
	$0 \leqq k \leqq 25$	$0 \leqq k \leqq 8$
	$0 \leqq l \leqq 9$	$-23 \leqq l \leqq 23$
Variation of five standard reflections $\sum(\lvert F_o \rvert / \lvert F_o \rvert_{\text{initial}})/5$	0.995—1.005	0.995—1.007
Number of reflections measured	5789	4671
Number of reflections observed [$\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$]	2639	2507
Transmission factor, A	0.79—0.85	0.73—0.84
Number of unique reflections, R_{int}	2446 (0.012)	2416 (0.013)
Number of parameters refined	449	297
R	0.063	0.068
wR	0.085	0.086
S	3.5	3.1
$(\Delta/\sigma)_{\max}$ for nonhydrogen atoms	0.118	0.258
ρ/e Å^{-3}	−0.41, 0.92	−0.37, 0.65

Table 2. Fractional Coordinates(×10^4) and Equivalent Isotropic Temperature Factors (×10)$^{6)}$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(1)					**(2)**				
Co	1381(1)	1138(1)	1113(2)	30	Co	2459(1)	1179(2)	651(1)	35
Cl(1)	957(2)	520(1)	−1120(3)	36	Cl(1)	2161(1)	−987(3)	1279(1)	48
Cl(2)	1770(2)	1739(1)	3315(3)	46	Cl(2)	2746(1)	3253(3)	−22(1)	50
N(1)	2511(4)	598(3)	1757(8)	48	N(1)	3389(4)	1723(9)	1612(4)	37
N(2)	2030(4)	1728(3)	−198(8)	51	N(2)	2897(4)	−858(10)	277(4)	48
N(3)	254(5)	1632(3)	334(10)	57	N(3)	1511(4)	753(10)	−270(4)	49
N(4)	741(5)	556(3)	2362(9)	55	N(4)	1922(4)	2915(10)	1007(4)	44
C(1)	2727(6)	1463(4)	−1126(12)	59	C(1)	3720(5)	−872(13)	411(5)	52
C(2)	1297(6)	2082(4)	−1344(12)	61	C(2)	2357(6)	−1160(16)	−536(5)	67
C(3)	550(6)	2236(4)	−278(14)	72	C(3)	1574(6)	−1057(15)	−579(6)	66
C(4)	−437(6)	1747(4)	1429(13)	65	C(4)	804(5)	977(15)	−196(6)	65
C(5)	−763(7)	1136(5)	2057(14)	72	C(5)	642(6)	2944(16)	−102(7)	73
C(6)	4(7)	791(5)	3241(12)	71	C(6)	1347(6)	4098(14)	420(6)	61
C(7)	1456(6)	192(4)	3484(12)	63	C(7)	2516(5)	4076(12)	1607(5)	52
C(8)	2187(6)	14(4)	2486(11)	56	C(8)	3127(5)	2709(12)	2125(4)	44
C(9)	3364(5)	861(4)	2782(11)	51	C(9)	4062(5)	2678(12)	1585(5)	44
C(10)	4242(6)	509(4)	2528(11)	59	C(10)	4791(5)	2159(16)	2288(5)	62
C(11)	5106(6)	775(4)	3646(11)	62	C(11)	5462(6)	2993(19)	2229(7)	91
C(12)	6032(7)	483(5)	3332(14)	76	C(12)	6229(7)	2342(21)	2837(7)	106
C(13)	6265(7)	613(4)	1656(13)	46	C(13)	6450(9)	453(20)	2770(7)	111
C(14)	6495(6)	1292(5)	1440(13)	71	C(14)	6412(11)	−149(34)	2060(11)	196
C(15)	6636(7)	1462(5)	−274(13)	80	C(15)	6454(10)	−2134(24)	1966(12)	170
C(16)	5753(8)	1370(5)	−1626(13)	80	C(16)	6129(8)	−2969(23)	1291(8)	117
C(17)	4864(7)	1704(4)	−1308(12)	43	C(17)	5339(9)	−2429(31)	766(14)	203
C(18)	4016(7)	1655(4)	−2654(11)	41	C(18)	4832(9)	−2950(26)	559(14)	207
C(19)	3136(6)	1930(4)	−2214(11)	58	C(19)	3919(6)	−2660(16)	151(7)	77
Cl(3)	−1557(2)	1777(1)	−3590(3)	52	Cl(3)	4380(1)	7637(4)	2971(2)	58
O(1)	−1414(6)	1384(4)	−2203(10)	35	O(1)	4132(6)	6182(11)	3274(5)	104
O(2)	−1504(8)	2401(5)	−3055(14)	65	O(2)	4034(6)	9247(13)	3088(5)	112
O(3)	−795(10)	1729(7)	−4330(16)	92	O(3)	4153(7)	7565(13)	2194(5)	124
O(4)	−2418(8)	1700(6)	−4549(16)	90	O(4)	5106(5)	8023(20)	3331(8)	192

Table 3. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°)

	1	2
Co-Cl(1)	2.275(3)	2.252(3)
Co-Cl(2)	2.228(3)	2.253(3)
Co-N(1)	2.011(6)	2.015(6)
Co-N(2)	2.024(7)	2.026(9)
Co-N(3)	1.967(7)	1.976(6)
Co-N(4)	1.974(8)	1.973(9)
Cl(1)-Co-Cl(2)	178.9(1)	177.3(1)
N(1)-Co-N(2)	93.8(3)	97.8(3)
N(1)-Co-N(4)	86.3(3)	86.6(3)
N(2)-Co-N(3)	85.8(3)	85.8(3)
N(3)-Co-N(4)	94.0(3)	89.7(3)

Table 4. Interatomic Hydrogen Bonds

A······H-B	l/Å		
	A····B	A····H	H-B
(1)			
O(2)····N(1)	3.14(1)	2.10(7)	1.06(7)
O(1)····N(4)	2.95(1)	2.10(7)	1.05(7)
(2)			
O(2)····N(1)	3.19(1)	2.39(8)	0.93(8)

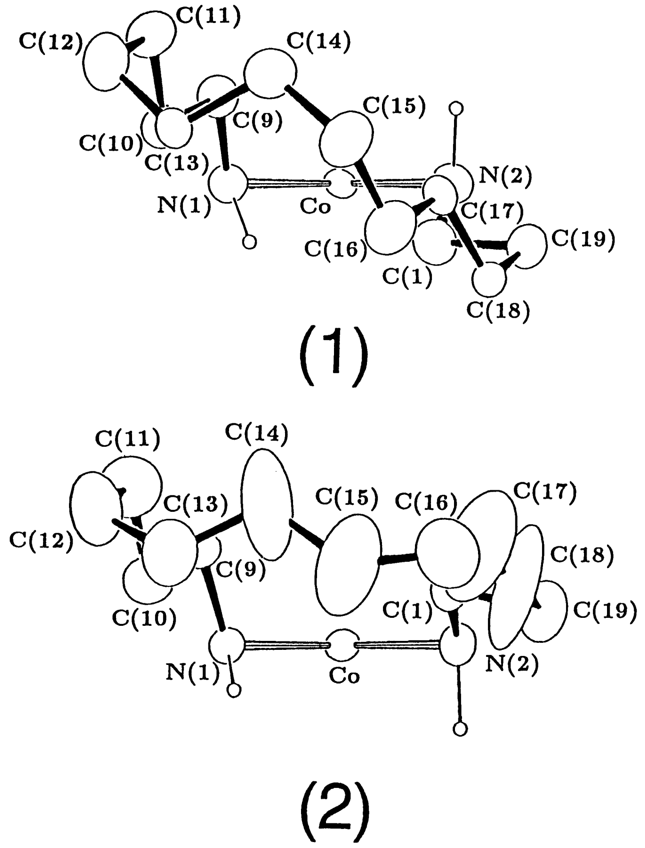


Fig. 3. The edge-on views of the fifteen-membered chelate rings.

Results and Discussion

Molecular Structure. Perspective views of the complex cations are presented in Fig. 2. The relative configurations of the secondary nitrogen atoms of the

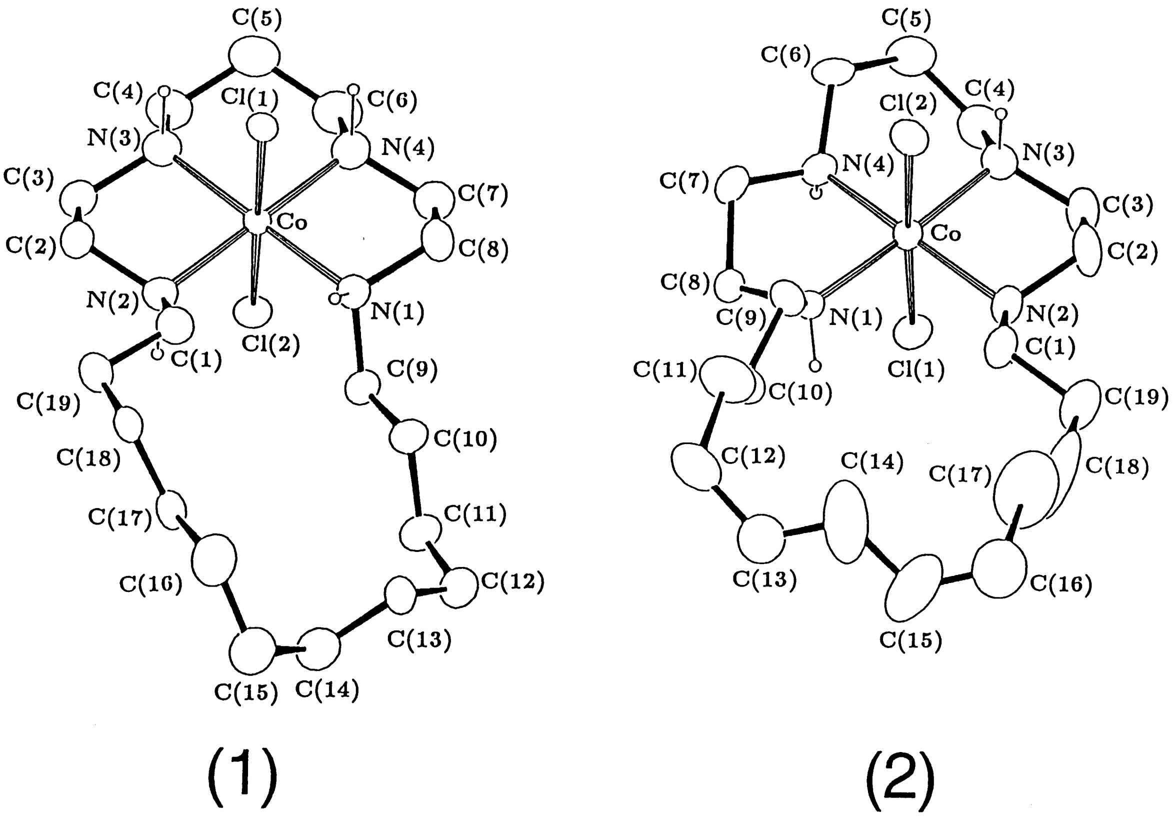


Fig. 2. The structures of the *trans*-$[CoCl_2(232N_415)]^+$ complex cations.

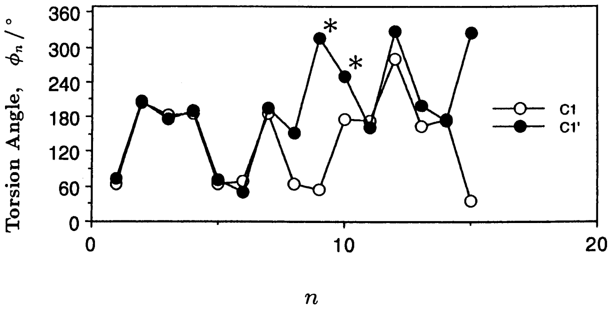


Fig. 4. The endocyclic torsion angles of the fifteen-membered chelate ring, ϕ_1=N(2)-Co-N(1)-C(9), ϕ_2=Co-N(1)-C(9)-C(10), and so on. Open and closed circles are for **1** and **2**, respectively. Asterisks indicated that the values of ϕ_9 and ϕ_{10} for **2** have low accuracy due to the disorder.

232N$_4$15 ligand are **(1)** *RRSR*(*SSRS*) and **(2)** *SSSR*(*RRRS*), where the four symbols (*R* or *S*) denote chirality at the nitrogen atoms in the order of N(2), N(3), N(4), and N(1). The assignment of the isomers based on the ^{13}C NMR and absorption spectra was confirmed. The six-membered chelate ring takes a chair form in **1** and a twist-boat form in **2**, as the result of different dispositions of the C atoms bonded to two N atoms in the six-membered chelate ring. The side views of the fifteen-membered chelate rings are presented in Fig. 3. The two N–C bond axes at N(1) and N(2) atoms can be denoted as *trans* and *cis* in **1** and **2**, respectively. The large ellipsoids of the carbon atoms from C(14) to C(18) in **2** suggest conformational disorder of the chelate ring. In general, flexibility of a ring increases with the ring size, hence, the fifteen-membered chelate ring would have a large number of stable configurations.[7] However, half of the carbon chain of the fifteen-membered chelate ring, from C(9) to C(15), takes almost the same form in **1** and **2**. The endocyclic torsion angles of the fifteen-membered ring are compared in Fig. 4. The torsion angles of Co–N–C–C and N–C–C–C, ϕ_2, ϕ_3, ϕ_{13}, and ϕ_{14}, are nearly 180°, indicating that the chain of the fifteen-membered ring near the metal center stretches. It is a great interest that the fifteen-membered chelate rings in **1** and **2** have such a similarity. The chelate angles of the fifteen-membered ring, N(1)-Co-N(2), are **(1)** 93.8(3)° and **(2)** 97.8(3)°. It seems that the chelate angles of the macrocyclic ligand are determined mainly by the small-sized rings, i.e. the chelate angles of the five- and six-membered rings have certain values with little flexibilities. In *trans*-[CoCl$_2$(222N$_4$8)]$^+$,[8] and *trans*-[Co(NO$_2$)$_2$(222N$_4$10)]$^+$,[9] the planar arrangement of three five-membered chelate rings causes fairly large distortion in the coordination of the remaining medium-sized ring moiety. In the present complex, a six-membered chelate ring replaces one of three five-membered chelate rings. The distortions in the chelate angles decreased as expected, but those in the Co–N bond distances remain. In **1** and **2**, the Co–N(1) and Co–N(2) bond lengths are longer by ca. 0.05 Å than the Co–N(3) and Co–N(4) bond distances.

Relative Stability of Isomers. Isomerization from the C$_1$' to the C$_1$ isomer occurs for *trans*-[CoCl$_2$(232N$_4$15)]$^+$ in basic solutions.[1] This fact suggests that the C$_1$ isomer is more stable than the C$_1$' isomer. Following factors may determine the stability of the isomers:

(1) Shape of the six-membered ring, i.e. the chair form (with *cis* disposition of the N–C axes) is preferable than the skew-boat form (with *trans* disposition). The six-membered chelate rings of cyclam, which is symbolized as 232N$_4$6, take chair forms and the conformation of the *trans* isomers of first-transition metal complexes is the Cs-type in Fig. 1.[10]

(2) Disposition of the N–C axes in the fifteen-membered ring, i.e. *trans* is preferable than *cis*. The chelate angle of the fifteen-membered ring in **2** is larger by 4.0(3)° than that in **1**. This fact may suggest the stronger intra steric-repulsions for the large-sized ring with *cis* disposition than *trans*.

(3) Disposition of the N–C axes in the five-membered ring, i.e. *trans* is preferable than *cis*. For *trans*-[CoCl$_2$(222N$_4$7)]$^+$, two isomers were obtained and the isomerization was observed from the C$_1$' to the C$_2$ isomer.[11] The stability of the C$_2$ isomer for 222N$_4$X complexes is explained by the *cis* dispositions of the N–C axes in the linking three five-membered rings.

Part of this study was met by a Scientific Research Grant from the Ministry of Education, Science and Culture, to which the authors' thanks are due.

References

1) M. Tsuchimoto, Y. Ito, and J. Fujita, in preparation.

2) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

3) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV. (Present distributor D. Reidel, Dordrecht)

4) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

5) Tables of the coordinates of hydrogen atoms, the bond lengths and bond angles, the anisotropic thermal parameters of the non-hydrogen atoms, and the observed and calculated structure factors are kept as Document No. 9023 at the Office of the Editor of Bull. Chem. Soc. Jpn.

6) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

7) H. Goto and E. Osawa, *J. Am. Chem. Soc.*, **111**, 8950 (1989).

8) M. Tsuchimoto, H. Takazawa, M. Kita, M. Nonoyama, S. Ohba, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 785 (1990).

9) M. Tsuchimoto, M. Kita, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **64**, 2554 (1991).

10) N. W. Alock, A. Berry, and P. Moore, *Acta Crystallogr., Sect. C*, **48**, 16 (1992).

11) M. Tsuchimoto, M. Kita, M. Nonoyama, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 227 (1990).